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CH DE FR GB IT LI SE(71) Applicant: Japan Tobacco Inc.  
2-1 Toranomon, 2-Chome  
Minato-Ku Tokyo 105(JP)(72) Inventor: Matsushita, Hajime 301 Nihon Tabako-  
Umegaoka-Daiichi-Apt. 39-9, Umegaoka  
Midori-ku Yokohama-shi(JP)(72) Inventor: Takahashi, Kyoko  
1-12-19, Setagaya  
Setagaya-ku Tokyo(JP)(72) Inventor: Shibagaki, Makoto 403 Nihon Tabako-  
Tsuchihashi-Daiichi-Apt. 5-6-1, Tsuchihashi  
Miyamae-ku Kawasaki-shi(JP)(74) Representative: Popp, Eugen, Dr. et al,  
MEISSNER, BOLTE & PARTNER Widenmayerstrasse 48  
Postfach 86 06 24  
D-8000 München 86(DE)

(54) A process of reduction of aldehydes and ketones.

(57) Disclosed is a process of reduction of aldehydes or ketones by means of reaction with alcohols, in the presence of a catalyst, to produce alcohols which correspond to said respective aldehyde or ketone. A solid of partially dehydrated one or more metal hydroxides whose metal is selected from the group consists of titanium, tin, iron, aluminium, cerium, and niobium is used as the catalyst. This process can be conducted either in a gas phase or in a liquid phase.

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A process of reduction of aldehydes and ketones

The present invention relates to a process of reduction of aldehydes or ketones, and more particularly, to a process of reduction which is conducted either in a gas phase or in a liquid phase by using a solid catalyst to obtain corresponding alcohols.

The Meerwein-Ponndorf-Verley reduction process is well known and has been widely used for reduction of aldehydes or ketones, to obtain corresponding alcohols.

In this process, aldehyde or ketone is subjected to reaction in the presence of metal alcoholate and alcohol. A number of combinations of metal alcoholates and alcohols have been tried, in order to attain an optimum result, of which the combination of aluminium isopropoxide and 2-propanol has proved to be most effective, due to it having the following advantages:

Firstly, the reaction using aluminium isopropoxide and 2-propanol is accompanied by hardly any adverse side reaction, such as aldol condensation.

Secondly, since aluminium isopropoxide is soluble not only in alcohol but also in hydrocarbon compounds, the reaction can be conducted in a homogeneous state.

Thirdly, since the reaction proceeds quite rapidly, a high yield of the reduction product can be realized.

Nevertheless, the process is accompanied by certain disadvantages. Since the above-described known process consists in a homogeneous reaction, it requires complex

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and painstaking follow-up operations including hydrolysis, extraction using an organic solvent, dehydration and distillation, so as to isolate the product after the completion of the reaction.

5        Moreover, since the carbonyl group of the starting compound is converted to a hydroxyl group in the final product of the reaction, its hydrophilic property is significantly enhanced as compared with that of the starting compound.

10       Therefore, the ratio of the part of the product that can be extracted from the aqueous layer, by means of an organic solvent, to the overall product will be inevitably held at a relatively low level, resulting in a poor yield of the reaction product.

15       Besides, whereas active aluminium isopropoxide is of trimer type, any aluminium isopropoxide now available in the market and/or which is supplied in a crystal form is of tetramer type and has poor catalytic activity. Therefore, a catalyst to be used for this process should  
20       be prepared immediately before the initiation of the reduction process.

What is more, catalysts which can be used for this process require particular care in their storage, because during storage they can be gradually hydrolyzed  
25       by water moisture in the air, and become aluminium hydroxide which has no catalytic activity.

Furthermore, in this process, catalyst which has been used should be hydrolyzed so as to isolate the product from the reaction system, upon completion of the  
30       reaction. As a result, it cannot be used further.

It is therefore the object of the present invention to provide a process of reduction of aldehydes or ketones, in the presence of a catalyst, to obtain corresponding alcohols at a high yield, characterized in that  
35       the process uses a catalyst which has high catalytic activity and can be used in a heterogeneous system at relatively low cost, that neither requires any complex

and painstaking follow-up operations for isolation of the product nor is accompanied by any deactivation problems due to water, and where the reaction can be conducted either in a gas phase or in a liquid phase.

5 To attain the above-mentioned object, the present invention provides a process of reduction of aldehydes or ketones by reaction with alcohols, in the presence of a catalyst, to obtain corresponding alcohols, characterized in that the catalyst is a solid of one or more  
10 partially dehydrated metal hydroxides whose metal is selected from the group consisting of titanium, tin, iron, aluminium, cerium, and niobium.

The present invention is characterized in that the catalyst which is used in the above process is a solid  
15 of one or more partially dehydrated metal hydroxides whose metal is selected from the group consisting of titanium, tin, iron, aluminium, cerium, and niobium. It should be noted that the inventors of the present invention have already found that a partially dehydrated  
20 solid of zirconium hydroxide can be used as a catalyst for the above process, and have already applied for a patent therefor (PCT/JP 86/00460).

The partially dehydrated metal hydroxide can be obtained by thermally treating the corresponding metal  
25 hydroxide under the condition in which the metal hydroxide has not yet fully dehydrated to become the corresponding metal oxide. In the case of zirconium, as described in the above international patent application, whereas zirconium hydroxide is completely dehydrated to  
30 become zirconia ( $ZrO_2$ ) when thermally treated at  $500^\circ C$  under atmospheric pressure, it will become partially dehydrated if treated at around  $300^\circ C$  and the partially dehydrated state is maintained in a stable manner. In other words, when zirconium hydroxide is treated at an  
35 intermediate temperature of about  $300^\circ C$ , the overall reaction system shows a reduction of weight by some 17% within one hour from the start of the reaction, the

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weight thereafter remaining at about the same level. This phenomenon can be observed not only in the partial dehydration of zirconium hydroxide but also in any corresponding partial dehydration of hydroxide of metals other than zirconium.

5 The catalyst compounds as described above are white and highly solid but amorphous. Hence, X-ray diffraction cannot be used for structural analysis of the materials, and as a result, their exact chemical structures are not known to date. However, the fact that these metal hydroxides can be partially dehydrated suggests that every product compound has a metal-oxygen-metal bonding, and that the hydroxyl groups which are directly bonded to the metal atom in the original material still remain. The catalyst materials described above are soluble neither in organic solvents such as alcohol nor in water, and are stable enough to function as heterogeneous catalysts. It is known that the materials have a relatively low surface acidity and ion exchangeability in the presence of various sources of ions.

20 The catalysts can be prepared in a relatively simple and inexpensive way by converting oxides, chlorides, or salts of their respective metals (which are found abundantly in nature as mineral resources) to hydroxides, which are in turn thermally treated in the respective predetermined conditions. This confers a significant advantage on the catalysts of the present invention, over any existing metal alcoholate catalysts. Furthermore, it should be noted that the catalyst materials of the present invention can be crushed to particles of suitable sizes for use or, alternatively, they can be carried by appropriate carrier substrate including alumina, active charcoal, silica gel, silica-alumina, and zeolite.

35 The process of reduction of aldehydes or ketones according to the present invention can be conducted

either in a gas phase or in a liquid phase.

When the process of the present invention is conducted in a liquid phase, it may be regarded simply as a process which is similar to the known Meerwein-Ponndorf-Verley process in which the catalyst of metal alcoholate is replaced by an catalyst of a solid of partially dehydrated metal hydroxide. Hence, any of the facilities and techniques which are used for the reduction of aldehydes or ketones in the known process may be used unchanged for the process of the present invention. For example, a distillation facility is used in the known process to separate acetone, which is produced as a by-product, in order to accelerate the reaction, and it can be used in the process according to the present invention, without any alterations thereto.

When reduction of aldehydes or ketones is conducted by the process of the present invention, in a liquid phase, 0.1 to 10 g, preferably 1 to 3 g, of any one of the above-mentioned catalyst materials is used for every 10 mmol of aldehyde or ketone. The catalyst is dissolved in 0.5 to 20 ml, preferably 5 to 10 ml, of 2-propanol or any other suitable alcohol, and the solution is mixed with the given aldehyde or ketone, the resultant mixture is then heated. During the reaction, acetone which is produced as a by-product is desirably removed by distillation, so that the speed of the reaction may be accelerated.

When the reaction is completed, the catalyst material is collected by means of filtration. The filtered solution is dried and then distilled to isolate the product. Depending on the circumstances, the product can be alternatively isolated through crystallization, directly from the solution. The collected catalyst material may be reutilized after being washed with ethanol and water, and then dried.

Since the above-described catalysts which can be used for the process of the present invention are highly

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active, but stable and hard amorphous substances, the process of the present invention can be realized in a gas phase, in the following way:

5 Firstly, a given amount of any of the above-described catalyst materials is placed in a suitable reaction tube, to provide a catalyst bed. Then, the reaction tube is heated to a temperature suitable for the expected reaction to take place; normally somewhere between 70°C and 200°C. After heating the tube, a mixture of aldehyde or ketone and alcohol is continuously  
10 fed into the reaction tube, in such a manner that the mixture comes into contact with the catalyst bed.

Air, nitrogen, helium, argon, or any other appropriate carrier gas may be used to feed in the mixture of the above-mentioned materials. A cooling device using water, ice, or some other cooling medium is provided at the exit of the reaction tube, so as to liquefy the gaseous reaction product and collect it. Although the collected liquid may contain a certain amount of  
15 residual materials and, in some case, of by-products other than the reaction product, the latter can be easily isolated, as in the case of reaction carried out in a liquid phase.  
20

The process of reduction of aldehydes or ketones according to the present invention is free from the problems which are associated with the conventional homogeneous catalyst reaction processes. Consequently, the corresponding alcohols can be produced at a relatively high yield. Moreover, the catalytic activity of the catalysts which can be used in the process according to the present invention will not deteriorate even when they are used continuously over a long period of time. Hence, the catalysts can be repeatedly used, so with the result that the process is free from emission of  
25 industrial wastes, thereby making it highly advantageous for industrial applications.  
30  
35

Some examples of the preparation of catalysts to be

used for the process of the present invention and of the reduction of aldehydes or ketones, according thereto will now be described.

Example 1 (preparation of an catalyst)

5        190 g of titanium tetrachloride was added 4 l of  
deionized water and then 28% aqueous ammonia was gradually added to the above mixture until pH of the solution was reached to 7.0. As the result, hydrated gel of the titanium hydroxide was produced. The hydrated gel  
10        was separated through filtration by using a Buchner funnel and then washed with deionized water repeatedly until no chloride ion was detected in the filtered solution. The gel thus obtained was then cut to small pieces by using a knife and they were scattered on a  
15        glass plate and dried at room temperature. When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various granular sizes. The mixture of water and granules were then filtered and the granules of titanium hydroxide which  
20        were separated from the water were dried in a enamelled vat at room temperature. The dried granules of titanium hydroxide were then sieved and those having the granular sizes between 24 and 60 meshes were selected. The selected granules were thermally treated in a drying  
25        container at 300°C for three hours thereby obtaining a solid of partially dehydrated titanium hydroxide.

Example 2 (preparation of a catalyst)

30        261 g of tin tetrachloride was added to 4 l of deionized water drop by drop. Immediately thereafter, 28% aqueous ammonia was gradually added to the mixture until pH = 7.0 was attained, thereby producing hydrated gel of tin hydroxide. The produced hydrated gel was then separated from the water through filtration using a Buchner funnel and the obtained hydrated gel was washed  
35        with deionized water until no chloride ion was detected in the filtered water. The gel thus obtained was then cut to small pieces by using a knife and they were



scattered on a glass plate and dried at room temperature. When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various sizes. The mixture of water and granules were then  
5 filtered and the granules which were separated from the water were then dried in a enamelled vat at room temperature. The dried granules of tin hydroxide were then sieved and those having the granular sizes between 24 and 60 meshes were selected. The selected granules were  
10 thermally treated in a drying container at 300°C for three hours thereby obtaining a solid of partially dehydrated thin hydroxide.

Example 3 (preparation of a catalyst)

270 g of ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was added  
15 drop by drop to 4 l of deionized water. Immediately thereafter, 28% aqueous ammonia was slowly added to the above mixture until pH = 7.0 was attained, then hydrated gel of ferric hydroxide was produced. The produced  
20 hydrated gel was separated through filtration by using a Buchner funnel and then washed with deionized water repeatedly until no chloride ion was detected in the filtered solution. The hydrated gel thus obtained was cut to small pieces by using a knife and they were scattered on a glass plate and dried at room temperature.  
25 When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various sizes. The mixture of water and granules were then filtered and the granules which were separated from the water were dried in a enamelled vat at room temperature.  
30 The dried granules of ferric hydroxide were then sieved and those having the granular sizes between 24 and 60 meshes were selected. The selected granules were thermally treated in a drying container at 300°C for three hours thereby obtaining a solid of partially dehydrated  
35 ferric hydroxide.

Example 4 (preparation of a catalyst)

328 g of sodium aluminate was dissolved in 3 l of

deionized water. Then 2 l of aqueous solution containing 336 g of sodium hydrogencarbonate was gradually added to the above solution while it was kept stirring until hydrated gel of the sodium aluminate was produced. The produced hydrated gel was separated through filtration and then washed with deionized water repeatedly until the pH of the washing water reached 7.5. The hydrated gel thus obtained was then cut to small pieces by using a knife and they were scattered on a glass plate and dried at room temperature. When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various sizes. The mixture of water and granules were then filtered and the granules of aluminium hydroxide which were separated from the water were then dried in a enamelled vat at room temperature. The dried granules of aluminium hydroxide were then sieved and those having the granular sizes between 24 and 60 meshes were selected. The selected granules were thermally treated in a drying container at 300° for three hours thereby obtaining a solid of partially dehydrated aluminium hydroxide.

Example 5 (preparation of a catalyst)

186 g of cerous chloride ( $\text{Ce}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ ) was dissolved in 2 l of deionized water and then 25 ml of 35% hydrogen peroxide solution was added to the above mixture for oxidization. Thereafter, 28% aqueous ammonia was gradually added to the oxidized solution while the latter was being stirred until the pH of the solution reached 7.0, then hydrated gel of ceric hydroxide was produced. The produced hydrated gel was separated through filtration and then washed with deionized water repeatedly until no chloride ion was detected in the washing water. The gel thus obtained was then cut to small pieces by using a knife and they were scattered on a glass plate and dried at room temperature. When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various granular size. The

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mixture of water and granules were then filtered and the granules of ceric hydroxide which were separated from the water were dried in a enamelled vat at room temperature. The dried granules of ceric hydroxide were then sieved and those having the granular size between 24 and 60 meshes were selected. The selected granules were thermally treated in a drying container at 300°C for three hours thereby obtaining a solid of partially dehydrated ceric hydroxide.

10 Example 6 (preparation of an catalyst)

50 g of niobium pentachloride anhydride was dissolved in 100 cc of concentrated hydrochloric acid and then the solution was diluted with 2 l of deionized water. The diluted solution was boiled for two hours thereby producing hydrated gel of niobium (V) hydroxide. The produced hydrated gel was washed with deionized water until no chloride ion was detected in the washing water. The hydrated gel thus obtained was then cut to small pieces by using a knife and they were scattered on a glass plate and dried at room temperature. When the dried pieces were introduced into deionized water, they were fiercely cracked to granules of various sizes. The mixture of water and granules were then filtered and the granules of niobium (V) hydroxide which were separated from the water were dried in an enamelled vat at room temperature. The dried granules of niobium (V) hydroxide were then sieved and those having the granular sizes between 24 and 60 meshes were selected. The selected granules were thermally treated in a drying container at 300°C for three hours thereby obtaining a solid of partially dehydrated niobium hydroxide.

Examples 7-21 (reduction reactions: gas phase)

Using a variety of partially dehydrated metal hydroxides which were prepared in such ways as described in Examples 1-6 above, reduction of aldehydes or ketones was conducted as follows.

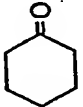
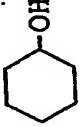
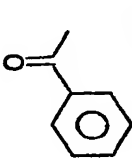
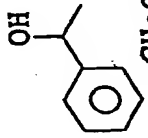
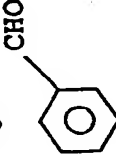
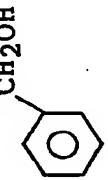
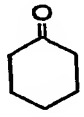
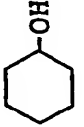
The amount of the catalyst used in every example

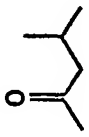
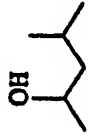

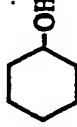

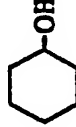
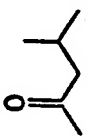
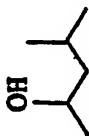
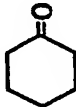
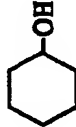
was 2 g.

5       The prescribed amount of any one of the catalysts  
as cited above was put into a glass tube (inner  
diameter = 4 mm, outer diameter = 6 mm) and the tube was  
10       fixedly mounted on an electric furnace. The glass tube  
served as a reactor vessel and liquid mixture of alcohol  
and an aldehyde or ketone which was to be reduced was  
fed into the tube by means of a micro-feeder at a rate  
of 5 ml/hour. A nitrogen gas flow (0.5 ml/sec) was  
10       utilized to carry the material. The alcohol used was  
cyclohexanol in Example 13, ethanol in Example 14 and  
2-propanol in the rest of the examples. The mol ratio  
of aldehyde or ketone to alcohol was 1:10 except for  
that of Example 10, in which the ratio of ketone to  
15       alcohol was 1:30.

20       The supplied material substances were gasified in  
the glass tube and put into contact with the catalyst  
for reaction. Then the reaction product came flowing  
out of the tube. The gaseous product was cooled with  
water for liquefaction for ease of collection and the  
liquefied product was subjected to a gas chromatography  
analysis to determine the conversion rate and the yield.  
Table 1 shows the results of the experiments conducted  
for the examples.

Table 1  
Reduction Reactions in a Gas Phase

No.	catalyst	material	reaction temperature (°)	product	conver- sion rate (%)	yield (%)
7	Example 1 (titanium)		100		22	15
8	"	"	150	"	44	44
9	"	"	200	"	99	92
10	"	"	150	"	62	62
11	"		150		67	67
12	"		150		82	41
13	"	"	150	"	94	36
14	"	"	150	"	39	30
15	Example 2 (tin)		100		60	60

No.	catalyst	material	reaction temperature (°)	product	conver- sion rate (%)	yield (%)
16	"		150		58	52
17	Example 3 (iron)		100		27	27
18	Example 4 (cerium)		100		72	68
19	"		150		65	55
20	Example 5 (aluminium)		100		39	39
21	Example 6 (niobium)	"	100	"	20	14

Examples 22-30 (reduction reactions: liquid phase)

Using a variety of partially dehydrated metal hydroxides which had been prepared in such ways as described in Example 1-6 above, aldehydes and ketones were reduced in a manner as described below.

5

The amount of the catalyst used in every example was 2 g.

The prescribed amount of any one of the catalysts as cited above was put into a flask having the volume of 50 ml which was equipped with a reflux device. 10 ml of liquid mixture of alcohol and an aldehyde or ketone which was to be reduced was put into the flask and set for reaction by heating with a mantle heater for five hours, during which the liquid mixture was slowly reflowed. The alcohol used was cyclohexanol in Example 22 and 2-propanol in the rest of the examples. The mol ratio of aldehyde or ketone to alcohol was 1:10. In Example 23, an equivalent amount of xylene was added to the reaction liquid and the mixture was subjected to reflux.

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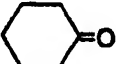
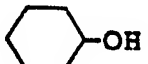
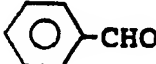
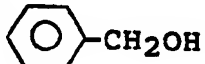
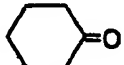
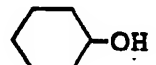
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After completion of reaction, a small amount of the liquid product was taken out as sample and subjected to a gas chromatography analysis to determine the conversion rate and the yield. Table 2 shows the results of the experiments conducted for the examples.

25

Table 2  
Reduction Reactions in a Liquid Phase

No.	catalyst	material	product	con- ver- sion rate (%)	yield (%)
22	Example 1 (titanium)			17	14
23	"	"	"	20	20
24	"			40	15
25	"	"	"	99	40
26	Example 2 (tin)			20	20
27	Example 3 (iron)	"	"	25	25
28	Example 4 (cerium)	"	"	45	32
29	Example 5 (aluminium)	"	"	6	6
30	Example 6 (niobium)	"	"	17	6



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## Claims:

1. A process of reduction of aldehydes or ketones by reaction with alcohols, in the presence of a catalyst, to produce alcohols which correspond to said respective aldehyde or ketone, characterized in that  
5 said catalyst is a solid of one or more partially dehydrated metal hydroxides whose metal is selected from the group consisting of titanium, tin, iron, aluminium, cerium, and niobium.
2. A process of reduction of aldehydes or ketones  
10 according to claim 1, characterized in that said partially dehydrated solid of metal hydroxides are carried by a suitable carrier substance.
3. A process of reduction of aldehydes or ketones according to claim 1 or claim 2, characterized in that  
15 said partially dehydrated solid of metal hydroxides is repeatedly used.
4. A process of reduction of aldehydes or ketones according to one of claims 1 to 3, characterized in that the reduction reaction is conducted in a liquid phase,  
20 and said catalyst is recovered by means of filtration, after completion of the reaction.
5. A process of reduction of aldehydes or ketones according to claim 4, characterized in that a suitable solvent is used with the reaction material.
- 25 6. A process of reduction of aldehydes or ketones according to one of claims 1 to 3, characterized in that a catalyst bed is prepared by placing said catalyst in a suitable reaction tube, and continually feeding a reactant material thereinto, to cause the reaction to take  
30 place by the reactant material coming into contact with the catalyst bed, the reaction product being then collected at the exit of said reaction tube, by way of condensation.

7. Alcohols produced by a process of reduction of aldehydes or ketones according to one of the preceeding claims.

(19)



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CH DE FR GB IT LI SE(71) Applicant: Japan Tobacco Inc.  
2-1 Toranomon, 2-Chome  
Minato-Ku Tokyo 105(JP)(72) Inventor: Matsushita, Hajime 301 Nihon Tabako-  
Umeaoka-Daiichi-Apt. 39-9, Umeaoka  
Midori-ku Yokohama-shi(JP)(72) Inventor: Takahashi, Kyoko  
1-12-19, Setagaya  
Setagaya-ku Tokyo(JP)(72) Inventor: Shibagaki, Makoto 403 Nihon Tabako-  
Tsuchihashi-Daiichi-Apt. 5-6-1, Tsuchihashi  
Miyamae-ku Kawasaki-shi(JP)(74) Representative: Popp, Eugen, Dr. et al,  
MEISSNER, BOLTE & PARTNER Widenmayerstrasse 48  
Postfach 86 06 24  
D-8000 München 86(DE)

(54) A process of reduction of aldehydes and ketones.

(57) Disclosed is a process of reduction of aldehydes or ketones by means of reaction with alcohols, in the presence of a catalyst, to produce alcohols which correspond to said respective aldehyde or ketone. A solid of partially dehydrated one or more metal hydroxides whose metal is selected from the group consists of titanium, tin, iron, aluminium, cerium, and niobium is used as the catalyst. This process can be conducted either in a gas phase or in a liquid phase.

**EP 0 239 993 A3**



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 183 225 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD) * Page 6, line 1 page 7, line 14; pages 9-10, example 1; pages 35-36, claims *	1,6,7	C 07 C 29/136 C 07 C 29/14 C 07 C 35/08 C 07 C 33/20
X,Y	US-A-3 551 497 (CH.E. WYMORE) * Column 1, lines 44-50; column 2, lines 32-52; column 4, example 11; columns 5-6; claims *	1,3,4,6,7	C 07 C 33/22 C 07 C 31/125
X,Y	JOURNAL OF ORGANIC CHEMISTRY, vol. 42, no. 7, 1st April 1977, pages 1202-1208, G.H. POSNER et al.: "Organic reactions at alumina surfaces.6. isopropyl alcohol and diisopropylcarbinol on dehydrated alumina as reagents for very selective carbonyl reductions" * page 1202; page 1203, table 1; page 1206 *	1,4,5,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 29/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30-11-1988	Examiner KINZINGER J.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

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